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(54) PROCESS FOR PRODUCING POLYETHYLENE

VERFAHREN ZUR HERSTELLUNG VON POLYETHYLEN

PROCEDE DE PRODUCTION DE POLYETHYLENE

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Description

FIELD OF INVENTION

[0001] The present invention relates to a polymerization process for the production of a polyethylene. Preferably the polyethylene has a reduced level of extractables. Films produced from the polyethylene are characterized by having improved strength properties.

BACKGROUND OF INVENTION

[0002] Polyethylene polymers are well known and are useful in many applications. In particular, linear polyethylene polymers possess properties which distinguish them from other polyethylene polymers, such as branched ethylene homopolymers commonly referred to as LDPE (low density polyethylene). Certain of these properties are described by Anderson et al, U.S. Patent No. 4,076,698.

[0003] A particularly useful polymerization medium for producing polyethylene polymers is a gas phase process. Examples of such are given in U.S. Patent Nos. 3,709,853; 4,003,712; 4,011,382; 4,302,566; 4,543,399; 4,882,400; 5,352,749 and 5,541,270 and Canadian Patent No. 991,798 and Belgian Patent No. 839,380.

[0004] Ziegler-Natta type catalyst systems for the polymerization of olefins are well known in the art and have been known at least since the issuance of U.S. Patent No. 3,113,115. Thereafter, many patents have been issued relating to new or improved Ziegler-Natta type catalysts. Exemplary of such patents are U.S. Patents Nos. 3,594,330; 3,676,415; 3,644,318; 3,917,575; 4,105,847; 4,148,754; 4,256,866; 4,298,713; 4,311,752; 4,363,904; 4,481,301 and Reissue 33,683.

[0005] These patents disclose Ziegler-Natta type catalysts that are well known as typically consisting of a transition metal component and a co-catalyst that is typically an organoaluminum compound. Optionally used with the catalyst are activators such as halogenated hydrocarbons and activity modifiers such as electron donors.

[0006] The use of halogenated hydrocarbons with Ziegler-Natta type polymerization catalysts in the production of polyethylene is disclosed in U.S. Patent No. 3,354,139 and European Patent Nos. EP 0 529 977 B1 and EP 0 703 246 A1. As disclosed, the halogenated hydrocarbons may reduce the rate of ethane formation, improve catalyst efficiency, or provide other effects. Typical of such halogenated hydrocarbons are monohalogen and polyhalogen substituted saturated or unsaturated aliphatic, alicyclic, or aromatic hydrocarbons having 1 to 12 carbon atoms. Exemplary aliphatic compounds include methyl chloride, methyl bromide, methyl iodide, methylene chloride, methylene bromide, methylene iodide, chloroform, bromoform, iodoform, carbon tetrachloride, carbon tetrabromide, carbon tetraiodide, ethyl chloride, ethyl bromide, 1,2-dichloroethane, 1,2-dibromoethane, methylchloroform, perchloroethylene and the like. Exemplary alicyclic compounds include chlorocyclopropane, tetrachlorocyclopentane and the like. Exemplary aromatic compounds include chlorobenzene, hexabromobenzene, benzotrichloride and the like. These compounds may be used individually or as mixtures thereof.

[0007] It is also well known, in the polymerization of olefins, particularly where Ziegler-Natta type catalysts are employed, to utilize, optionally, electron donors. Such electron donors often aid in increasing the efficiency of the catalyst and/or in controlling the stereospecificity of the polymer when an olefin, other than ethylene, is polymerized. Electron donors, typically known as Lewis Bases, when employed during the catalyst preparation step are referred to as internal electron donors. Electron donors when utilized other than during the catalyst preparation step are referred to as external electron donors. For example, the external electron donor may be added to the preformed catalyst, to the prepolymer, and/or to the polymerization medium.

[0008] The use of electron donors in the field of propylene polymerization is well known and is primarily used to reduce the atactic form of the polymer and increase the production ofthe isotactic polymers. The use of electron donors generally improves the productivity of the catalyst in the production of isotactic polypropylene. This is shown generally in U.S. Patent No. 4,981,930.

[0009] In the field of ethylene polymerization, where ethylene constitutes at least about 70% by weight of the total monomers present in the polymer, electron donors are utilized to control the molecular weight distribution (MWD) of the polymer and the activity of the catalyst in the polymerization medium Exemplary patents describing the use of internal electron donors in producing linear polyethylene are U.S. Patents Nos. 3,917,575; 4,187,385, 4,256,866; 4,293,673; 4,296,223; Reissue 33,683; 4,302,565; 4,302,566; and 5,470,812. The use of an external monoether electron donor, such as tetrahydrofuran (THF), to control molecular weight distribution is shown in U.S. Patent No. 5,055,535; and the use of external electron donors to control the reactivity of catalyst particles is described in U.S. Patent No. 5,410,002.

[0010] Illustrative examples of electron donors include carboxylic acids, carboxylic acid esters, alcohols, ethers, ketones, amines, amides, nitriles, aldehydes, thioethers, thioesters, carbonic esters, organosilicon compounds containing oxygen atoms, and phosphorus, arsenic or antimony compounds connected to an organic group through a carbon or oxygen atom.

SUMMARY OF THE INVENTION

[0011] The polymerization process of the present invention comprises the introduction into a polymerization medium containing ethylene and optionally at least one other olefin, a Ziegler-Natta type polymerization catalyst, tetrahydrofuran (THF) as an external electron donor and trimethylaluminum (TMA) as a co-catalyst. Optionally a halogenated hydrocarbon compound can be employed in the polymerization medium. The THF and/or the TMA may be added to the polymerization medium in any manner. The THF and/or the TMA may be added to the catalyst just prior to addition to the polymerization medium, or added separately from the catalyst to the polymerization medium in any manner known in the art. For example, the THF may optionally be premixed with the TMA co-catalyst.

[0012] If a gas phase fluidized bed process is utilized for polymerization of the ethylene, it may be advantageous to add the THF prior to the heat removal means, e.g., the heat exchanger, to slow the rate of fouling of said heat removal means.

[0013] All mention herein to elements of Groups of the Periodic Table are made in reference to the Periodic Table of the Elements, as published in "Chemical and Engineering News", 63(5), 27, 1985. In this format, the Groups are numbered 1 to 18.

DETAILED DESCRIPTION OF THE INVENTION

[0014] The present inventors have unexpectedly discovered that a particular combination of a Ziegler-Natta catalyst, trimethylaluminum (TMA) co-catalyst and tetrahydrofuran (THF) external electron donor makes it possible to produce a polyethylene in an improved manner. Preferably the resultant polyethylene has a reduced level of extractables. Furthermore, films produced from these polyethylenes unexpectedly have high impact resistance as typified by Dart Impact values and have a good balance of machine direction (MD) and transverse direction (TD) tear values.

[0015] The polymerization process of the present invention may be carried out using any suitable process. For example, there may be utilized polymerization in suspension, in solution, in super-critical or in the gas phase media. All of these polymerization processes are well known in the art.

[0016] A particularly desirable method for producing polyethylene polymers according to the present invention is a gas phase polymerization process preferably utilizing a fluidized bed reactor. This type reactor and means for operating the reactor are well known and completely described in U.S Patents Nos. 3,709,853; 4,003,712; 4,011,382; 4,012,573; 4,302,566; 4,543,399; 4,882,400; 5,352,749; 5,541,270; Canadian Patent No. 991,798 and Belgian Patent No. 839,380. These patents disclose gas phase polymerization processes wherein the polymerization medium is either mechanically agitated or fluidized by the continuous flow of the gaseous monomer and diluent. The entire contents of these patents are incorporated herein by reference.

[0017] In general, the polymerization process of the present invention may be effected as a continuous gas phase process such as a fluid bed process. A fluid bed reactor for use in the process of the present invention typically comprises a reaction zone and a so-called velocity reduction zone. The reaction zone comprises a bed of growing polymer particles, formed polymer particles and a minor amount of catalyst particles fluidized by the continuous flow of the gaseous monomer and diluent to remove heat of polymerization through the reaction zone. Optionally, some of the recirculated gases may be cooled and compressed to form liquids that increase the heat removal capacity of the circulating gas stream when readmitted to the reaction zone. A suitable rate of gas flow may be readily determined by simple experiment. Make up of gaseous monomer to the circulating gas stream is at a rate equal to the rate at which particulate polymer product and monomer associated therewith is withdrawn from the reactor and the composition of the gas passing through the reactor is adjusted to maintain an essentially steady state gaseous composition within the reaction zone. The gas leaving the reaction zone is passed to the velocity reduction zone where entrained particles are removed. Finer entrained particles and dust may be removed in a cyclone and/or fine filter. The gas is passed through a heat exchanger wherein the heat of polymerization is removed, compressed in a compressor and then returned to the reaction zone.

[0018] In more detail, the reactor temperature of the fluid bed process herein ranges from about 30°C to about 110°C. In general, the reactor temperature is operated at the highest temperature that is feasible taking into account the sintering temperature of the polymer product within the reactor.

[0019] The process of the present invention is suitable for the production of homopolymers of ethylene and/or copolymers, terpolymers, and the like, of ethylene and at least one or more other olefins. Preferably the olefins are alpha-olefins. The olefins, for example, may contain from 3 to 16 carbon atoms. Particularly preferred for preparation herein by the process of the present invention are linear polyethylenes. Such linear polyethylenes are preferably linear homopolymers of ethylene and linear copolymers of ethylene and at least one alpha-olefin wherein the ethylene content is at least about 70% by weight of the total monomers involved. Exemplary alpha-olefins that may be utilized herein are propylene, 1-butene, 1-pentene, 1-hexene, 1-heptene, 1-octene, 4-methylpent-1-ene, 1-decene, 1-dodecene, 1-hexadecene and the like. Also utilizable herein are polyenes such as 1,3-hexadiene, 1,4-hexadiene, cyclopentadiene, dicyclopentadiene, 4-vinylcyclohex-1-ene, 1,5-cyclooctadiene, 5-vinylidene-2-norbomene and 5-vinyl-2-norbornene, and olefins formed in situ in the polymerization medium. When olefins are formed in situ in the polymerization medium, the formation of linear polyethylenes containing long chain branching may occur.

[0020] The polymerization reaction of the present invention is carried out in the presence of a Ziegler-Natta type catalyst. In the process of the invention, the catalyst can be introduced in any manner known in the art. For example, the catalyst can be introduced directly into the polymerization medium in the form of a solution, a slurry or a dry free flowing powder. The catalyst can also be used in the form of a deactivated catalyst, or in the form of a prepolymer obtained by contacting the catalyst with one or more olefins in the presence of a co-catalyst.

[0021] The Ziegler-Natta catalysts are well known in the industry. The Ziegler-Natta catalysts in the simplest form are comprised of a transition metal compound and an organometallic co-catalyst compound. The metal of the transition metal compound is a metal of Groups 4, 5, 6, 7, 8, 9 and 10 of the Periodic Table of the Elements, as published in "Chemical and Engineering News", 63(5), 27, 1985. In this format, the groups are numbered 1-18. Exemplary of such transition metals are titanium, zirconium, vanadium, chromium, manganese, iron, cobalt, nickel, and the like, and mixtures thereof In a preferred embodiment the transition metal is selected from the group consisting of titanium, zirconium, vanadium and chromium, and in a still further preferred embodiment, the transition metal is titanium The Ziegler-Natta catalyst can optionally contain magnesium and chlorine. Such magnesium and chlorine containing catalysts may be prepared by any manner known in the art.

[0022] The co-catalyst added to the polymerization medium of the present invention is trimethylaluminum (TMA).

[0023] In the event that a prepolymerized form of the catalyst is to be employed then the organometallic co-catalyst compound used to form the prepolymer can be any organometallic compound containing a metal of Groups 1, 2, 11, 12, 13 and 14 of the above described Periodic Table of the Elements. Exemplary of such metals are lithium, magnesium, copper, zinc, boron, silicon and the like. However, when a prepolymer is employed, TMA is still utilized as the co-catalyst in the polymerisation medium

[0024] The catalyst system may contain conventional components in addition to the transition metal component, THF as external electron donor and the TMA co-catalyst component. For example, there may be added any internal electron donor(s) known in the art, any halogenated hydrocarbon(s), and the like.

[0025] The Ziegler-Natta catalyst may be prepared by any method known in the art. The catalyst can be in the form of a solution, a slurry or a dry free flowing powder. The amount or Ziegler-Natta catalyst used is that which is sufficient to allow production of the desired amount of the polyethylene.

[0026] In carrying out the polymerization process of the present invention, TMA is added to the polymerization medium in any amount sufficient to effect production of the desired polyethylene. It is preferred to incorporate the TMA in a molar ratio of TMA to transition metal component of the Ziegler-Natta catalyst ranging from about 1:1 to about 100:1. In a more preferred embodiment, the molar ratio of TMA to transition metal component ranges from about 1:1 to about 50:1.

[0027] In carrying out the polymerization process of the present invention THF as an external electron donor is added in any manner. For example, the THF may be added to the preformed catalyst, to the prepolymer during the prepolymerization step, to the preformed prepolymer and/or to the polymerization medium. The THF may optionally be premixed with the TMA co-catalyst. The THF is added in any amount sufficient to effect production of the desired polyethylene. It is preferred to incorporate the THF in a molar ratio of THF to transition metal component of the Ziegler-Natta catalyst ranging from about 0.01:1 to about 100:1. In a more preferred embodiment, the molar ratio of THF to transition metal component ranges from about 0.1:1 to about 50:1.

[0028] In carrying out the polymerization process of the present invention, there may be added other conventional additives generally utilized in processes for polymerizing olefins. Specifically there may be added any halogenated hydrocarbon, including those mentioned hereinbefore, and preferably, chloroform. The molar ratio of halogenated hydrocarbon to transition metal component ofthe Ziegler-Natta catalyst ranges preferably from about 0.001:1 to about 1:1.

[0029] The molecular weight of the polyethylene produced by the present invention can be controlled in any known manner, e.g., by using hydrogen. The molecular weight control may be evidenced by an increase in the melt index (I_2) of the polymer when the molar ratio of hydrogen to ethylene in the polymerization medium is increased.

[0030] The molecular weight distribution of the polyethylene produced by the present invention is expressed by the melt flow ratio (MFR). Preferably, the polyethylenes have MFR values varying from about 24 to about 34, and have densities ranging from about 0.880gm/cc to about 0.964gm/cc.

[0031] The polyethylenes of the present invention may be fabricated into films by any technique known in the art. For example, films may be produced by the well known cast film, blown film and extrusion coating techniques.

[0032] Further, the polyethylenes may be fabricated into other articles of manufacture, such as molded articles, by any of the well known techniques.

[0033] The invention will be more readily understood by reference to the following examples. There are, of course, many other forms of this invention which will become obvious to one skilled in the art, once the invention has been fully disclosed, and it will accordingly be recognized that these examples are given for the purpose of illustration only, and are not to be construed as limiting the scope of this invention in any way.

Examples

[0034] In the following examples the test procedures listed below were used in evaluating the analytical properties of the polyethylenes herein and in evaluating the physical properties of the films of the examples.

a) Dart Impact is determined according to ASTM D-1709, Method A; with a 38.1 mm dart having a smooth phenolic head, and a drop height of 0.66 meter. Film thickness of about 1 mil;
b) Machine Direction Tear, MD_{TEAR}(g/mil): ASTM D-1922
c) Transverse Direction Tear, TD_{TEAR}(g/mil): ASTM D-1922
d) Density is determined according to ASTM D-4883 from a plaque made according to ASTM D1928;
e) Melt Index (MI), I_2, is determined in accord with ASTM D-1238, condition E, measured at 190°C, and reported as decigrams per minute;
f) High Load Melt Index (HLMI), I_{21}, is measured in accord with ASTM D-1238, Condition F, measured at 10.0 times the weight used in the melt index test, I_2, above;
g) Melt Flow Ratio (MFR) = I_{21}/I_2 or High Load Melt Index/Melt Index;
h) Ether Extractable: A powder polymer sample approximately 100 grams in size is obtained from the reactor prior to any compounding stage. The sample is placed in a tared extraction thimble and weighed to the nearest 0.1mg. The extraction thimble containing the sample is then placed in a Soxhlet extractor and continuously extracted with ether for 6 hours. The extraction thimble containing the sample that has been extracted is then dried to a constant weight in a vacuum over a 2 hour time period. The ether extractable is then reported as the weight fraction of sample that dissolved in the ether normalized with respect to the original sample weight. For example, an Ether Extractable of 2 % indicates that 2 % by weight of the polymer was extracted by the ether; and
i) n-Hexane Extractable - is determined in accordance with 21 CFR 177.1520 (Option 2). More particularly, an approximately I square inch film test specimen having a thickness $\leq$ 4 mils weighing 2.5±0.05 grams is placed into a tared sample basket and accurately weighed to the nearest 0.1 milligram. The sample basket containing the test specimen is then placed in a 2-liter extraction vessel containing approximately 1 liter of n-hexane. The basket is placed such that it is totally below the level of n-hexane solvent. The sample resin film is extracted for 2 hours at 49.5 ± 0.5°C and then the basket is raised above the solvent level to drain momentarily. The basket is removed and the contents are rinsed by immersing several times in fresh n-hexane. The basket is allowed to dry between rinsing. The excess solvent is removed by briefly blowing the basket with a stream of nitrogen or dry air. The basket is placed in the vacuum oven for 2 hours at 80 ± 5°C. After 2 hours, it is removed and placed in a desiccator to cool to room temperature (about 1 hour). After cooling, the basket is reweighed to the nearest 0.1 milligram. The percent n-hexane extractable content is then calculated from the weight loss of the original sample.

[0035] The Ziegler-Natta catalyst used herein was prepared in accordance with Example 1-a of European Patent Application EP 0 703 246 A1.

[0036] The prepolymer used in Examples 1-7 herein was prepared in accordance with Example 1-b of European Patent Application EP 0 703 246 A1. A prepolymer containing about 34 grams of polyethylene per millimole of titanium was thus obtained.

[0037] The polymerization process utilized in Examples 1-7 herein was carried out in a fluidized-bed reactor for gas-phase polymerization, consisting of a vertical cylinder of diameter 0.9 meters and height 6 meters and surmounted by a velocity reduction chamber. The reactor is provided in its lower part with a fluidization grid and with an external line for recycling gas, which connects the top of the velocity reduction chamber to the lower part of the reactor, at a point below the fluidization grid. The recycling line is equipped with a compressor for circulating gas and a heat transfer means such as a heat exchanger. In particular the lines for supplying ethylene, an olefin such as 1-butene, 1-pentene and 1-hexene, hydrogen and nitrogen, which represent the main constituents of the gaseous reaction mixture passing through the fluidized bed, feed into the recycling line. Above the fluidization grid, the reactor contains a fluidized bed consisting of a polyethylene powder made up of particles with a weight-average diameter of about 0.5 mm to about 1.4 mm. The gaseous reaction mixture, which contains ethylene, olefin comonomer, hydrogen, nitrogen and minor amounts of other components, passes through the fluidized bed under a pressure ranging from about 290 psig to about 300 psig with an ascending fluidization speed, referred to herein as fluidization velocity, ranging from about 1.8 feet per second to about 2.0 feet per second.

[0038] Furthermore, in each of Examples 1-7, a catalyst as described above, in prepolymer form, is introduced intermittently into the reactor. The said catalyst contains magnesium, chlorine and titanium. The prepolymer form contains about 34 grams of polyethylene per millimole of titanium and an amount of tri-n-octylaluminum (TnOA) such that the molar ratio, A1/Ti, is equal to about 1.1:1. In Example 8, the Ziegler-Natta catalyst is introduced directly into the reactor without having been formed into a prepolymer. The rate of introduction of the prepolymer or catalyst into the reactor is adjusted for each given set of conditions in achieving the desired production rate. During the polymerization; a solution of trimethylaluminum (TMA) in n-hexane, at a concentration of about 2 weight percent, is introduced continuously into the line for recycling the gaseous reaction mixture, at a point situated downstream of the heat transfer means. The feed rate of TMA is expressed as a molar ratio of TMA to titanium (TMA/Ti), and is defined as the ratio of the TMA feed rate (in moles of TMA per hour) to the catalyst or prepolymer feed rate (in moles of titanium per hour). Simultaneously, a solution of chloroform ($CHCl_3$) in n-hexane, at a concentration of about 0.5 weight percent, is introduced continuously into the line for recycling the gaseous reaction mixture. The feed rate of $CHCl_3$ is expressed as a molar ratio of $CHCl_3$ to titanium ($CHCl_3$/Ti), and is defined as the ratio of the $CHCl_3$ feed rate (in moles of $CHCl_3$ per hour) to the catalyst or prepolymer feed rate (in moles of titanium per hour).

[0039] When an external donor is utilized in any of the following examples, it is THF. A solution of tetrahydrofuran (THF) in n-hexane, at a concentration of about 1 weight percent, can be introduced continuously into the line for recycling the gaseous reaction mixture. The feed rate of THF is expressed as a molar ratio or THF to titanium (THF/Ti), and is defined as the ratio of the THF feed rate (in moles of THE per hour) to the catalyst or prepolymer feed rate (in moles of titanium per hour).

[0040] The productivity of the catalyst or prepolymer (Productivity) is the ratio of pounds of polyethylene produced per pound of catalyst or prepolymer added to the reactor. The activity of the catalyst or prepolymer is expressed as grams of polyethylene per millimole titanium per hour per bar of ethylene pressure.

EXAMPLE 1

Preparation of LLDPE with TMA as Co-Catalyst and with THF as External Electron Donor

[0041] The process conditions are given in Table 1 and the resin properties are given in Table 2. The molar ratio of TMA to titanium was 7. The molar ratio of $CHCl_3$ to titanium was 0.06. The process was conducted with the addition of tetrahydrofuran (THF) as an external electron donor at a molar ratio of THE to titanium of 3. 1-Hexene was used as comonomer. Under these conditions a linear polyethylene free from agglomerate was withdrawn from the reactor at a rate of 206 lb/h (pounds per hour). The productivity of the catalyst was 179 pounds of polyethylene per pound of prepolymer which corresponds to an activity of 261 grams polyethylene per millimole titanium per hour per bar of ethylene partial pressure.

[0042] The linear polyethylene had a density of 0.918 g/cc and a melt index $MI_{2.16}$, I_2, of 0.9 dg/min. The Melt Flow Ratio, I_{21}/I_2, was 30 and the ether extractables were 2.8 % by weight. The dart impact was 530 g/mil and the MD_{TEAR} and TD_{TEAR} were 410 g/mil and 540 g/mil, respectively.

EXAMPLE 2 (COMPARATIVE)

Preparation of Linear Low Density Polyethylene (LLDPE) with TMA as co-catalyst

[0043] The process conditions are given in Table 1 and the resin properties are given in Table 2. The molar ratio of trimethylaluminum (TMA) to titanium was 3. The molar ratio of $CHCl_3$ to titanium was 0.03. The process was conducted without the addition of THF. 1-Hexene was used as comonomer. Under these conditions a linear polyethylene free from agglomerate was withdrawn from the reactor at a rate of 150 1b/h. The productivity of the catalyst was 375 pounds of polyethylene per pound of prepolymer which corresponds to an activity of 1154 grams of polyethylene per millimole of titanium per hour per bar of ethylene partial pressure.

[0044] The linear polyethylene had a density of 0.918 g/cc and a melt index $MI_{2.16}$, I_2, of 0.9 dg/min. The Melt Flow Ratio, I_{21}/I_2, was 33 and the ether extractables were 4.8 % by weight. The dart impact was 200 g/mil and the MD_{TEAR} and TD_{TEAR} were 450 g/mil and 500 g/mil, respectively.

EXAMPLE 3 (COMPARATIVE)

Preparation of LLDPE with TEAL as Co-Catalyst and with THF as External Electron Donor

[0045] The process conditions are given in Table 1 and the resin properties are given in Table 2. The molar ratio of triethylaluminum (TEAL) to titanium was 7. The molar ratio of $CHCl_3$ to titanium was 0.06. The molar ratio of THF to titanium was 3. 1-Hexene was used as comonomer. Under these conditions a linear polyethylene free from agglomerate was withdrawn from the reactor at a rate of 197 1b/h. The productivity of the catalyst was 122 pounds of polyethylene per pound of prepolymer which corresponds to an activity of 168 grams polyethylene per millimole titanium per hour per bar of ethylene partial pressure.

[0046] The linear polyethylene had a density of 0.918 g/cc and a melt index $MI_{2.16}$, I_2, of 0.9 dg/min. The Melt Flow Ratio, I_{21}/I_2, was 31 and the ether extractables were 3.6 % by weight. The dart impact was 260 g/mil and the MD_{TEAR} and TD_{TEAR} were 430 g/mil and 560 g/mil, respectively.

EXAMPLE 4 (COMPARATIVE)

Preparation of LLDPE with TEAL as Co-Catalyst and with THF as External Electron Donor

[0047] The process conditions are given in Table 1 and the resin properties are given in Table 2. The molar ratio of TEAL to titanium was 13. The molar ratio of $CHCl_3$ to titanium was 0.06. The molar ratio of THF to titanium was 3. 1-Hexene was used as comonomer. Under these conditions a linear polyethylene free from agglomerate was withdrawn from the reactor at a rate of 207 1b/h. The productivity of the catalyst was 150 pounds of polyethylene per pound of prepolymer which corresponds to an activity of 216 grams polyethylene per millimole titanium per hour per bar of ethylene partial pressure.

[0048] The linear polyethylene had a density of 0.918 g/cc and a melt index $MI_{2.16}$, I_2, of 0.9 dg/min. The Melt Flow Ratio, I_{21}/I_2, was 32 and the ether extractables were 4.0 % by weight. The dart impact was 190 g/mil and the MD_{TEAR} and TD_{TEAR} were 416 g/mil and 571 g/mil, respectively.

Table 1:

Reactor Conditions for Examples 1 through 4

	Example			
	1	2	3	4
Reactor Pressure (psig)	295	290	297	296
Reactor Temperature (°C)	86	84	86	86
Fluidization Velocity (ft/sec)	1.94	1.79	1.94	1.93
Fluidized Bulk Density (lb/ft^3)	15.8	17.0	15.6	15.9
Reactor Bed Height (ft)	11 1	9.4	11	11
Ethylene (C_2) (mole%)	28	38	28	28
H_2/C_2 (molar ratio)	0.152	0.178	0.160	0.134
1-Hexene/C_2 (molar ratio)	0.165	0.191	0.168	0.165
Co-catalyst	TMA	TMA	TEAL	TEAL
A1/Ti (molar ratio)	7	3	7	13
External Electron Donor	THF	---	THF	THF
THF/Ti (molar ratio)	3	---	3	3
$CHCl_3$/Ti	0.06	0.03	0.06	0.06
Production Rate (lb/h)	206	150	197	207
Space Time Yield (1b/h-ft^3)	4.05	3.59	3.80	4.08
Productivity (mass ratio)	179	375	122	150
Activity(g PE/mmoleTi-h-bar$_{ethylene}$)	261	1154	168	216
Residual Titanium (ppm)	8.6	1.1	12.3	9.5

Table 2:

Resin Properties for LLDPE prepared in Examples 1 through 4

	Example			
	1	2	3	4
Density (g/cc)	0.918	0.918	0.918	0.918
Melt Index, I2, (dg/min)	0.9	0.9	0.9	0.9
Melt Flow Ratio (I21/I2)	30	33	31	32
Ether Extractable (wt %)	2.8	4.8	3.6	4.0

Table 2: (continued)

Resin Properties for LLDPE prepared in Examples 1 through 4	Example			
	1	2	3	4
n-Hexane Extractable (wt%)	1.6	3.0	2.4	2.5
Dart Impact (g/mil)	530	200	260	190
MD_{TEAR}(g/mil)	410	450	430	416
TD_{TEAR} (g/mil)	540	500	560	571

[0049] A review of the data shown in Tables 1 and 2 reveal the unexpectedly superior results obtained for the polyethylene produced utilizing the process of the present invention, as shown in Example 1. More particularly, as shown in Example 1, wherein TMA and THF are both utilized in the polymerization process, a polyethylene is produced having a level of Dart Impact Strength more than twice as great as the polyethylene produced in Example 2 wherein TMA is utilized but in the absence of THF. Furthermore, as shown in Examples 3 and 4 wherein TEAL is utilized instead of TMA as co-catalyst, even together with THF, the resultant polyethylene has a Dart Impact Strength less than half that of the polyethylene produced in accordance with the process of the present invention as shown in Example 1. In addition to the foregoing, it will be noted from the data in Table 2 that the polyethylene produced in accordance with the present invention utilizing the specific combination of TMA and THF, is characterized by having a narrower molecular weight distribution, as evidenced by Melt Flow Ratio values, as compared with the polyethylene of Examples 2, 3 and 4. It is further to be noted that the extractable content of the polyethylene of the present invention (Example 1) is significantly lower than the extractable content of any of the comparative polyethylenes of Examples 2, 3 and 4. It is further to be noted that other physical properties ofthe polyethylenes of Examples 1, 2, 3 and 4 are substantially similar.

EXAMPLES 5-7

[0050] The following Examples 5, 6 and 7 are intended to demonstrate that similar results are obtainable when using olefins such as 1-butene, 1-pentene and 1-hexene as the comonomer with ethylene.

EXAMPLE 5

Preparation of a 0.908 Density LLDPE with TMA as Co-Catalyst. with THF as External Electron Donor and with 1-Hexene as Comonomer

[0051] The process conditions are given in Table 3 and the resin properties are given in Table 4. The molar ratio of TMA to titanium was 6. The molar ratio of $CHCl_3$ to titanium was 0.06. The molar ratio of THF to titanium was 3. 1-Hexene was used as comonomer. Under these conditions a linear polyethylene free from agglomerate was withdrawn from the reactor at a rate of 196 1b/h. The productivity of the catalyst was 168 pounds of polyethylene per pound of prepolymer which corresponds to an activity of 259 grams polyethylene per millimole titanium per hour per bar of ethylene partial pressure.

[0052] The linear polyethylene had a density of 0.908 and a melt index $MI_{2.16}$, I_2, of 0.6 dg/min. The Melt Flow Ratio, I_{21}/I_2, was 34 and the ether extractables were 5.2 % by weight. The dart impact was greater than 1500 g/mil and the MD_{TEAR} and TD_{TEAR} were 700 g/mil and 750 g/mil, respectively.

EXAMPLE 6

Preparation of a 0.908 Density LLDPE with TMA as Co-Catalyst with THF as External Electron Donor and with 1-Pentene as Comonomer

[0053] The process conditions are given in Table 3 and the resin properties are given in Table 4. The molar ratio of TMA to titanium was 7. The molar ratio of $CHCl_3$ to titanium was 0.06. The molar ratio of THF to titanium was 3. Under these conditions a linear polyethylene free from agglomerate was withdrawn from the reactor at a rate of 200 1b/h. The productivity of the catalyst was 129 pounds of polyethylene per pound of prepolymer which corresponds to an activity of 239 grams polyethylene per millimole titanium per hour per bar of ethylene partial pressure.

[0054] The linear polyethylene had a density of 0.908 and a melt index $MI_{2.16}$, I_2, of 0.5 dg/min. The Melt Flow Ratio, I_{21}/I_2, was 31 and the ether extractables were 3.1 % by weight.

EXAMPLE 7

Preparation of a 0.908 Density LLDPE with TMA as Co-Catalyst, with THF as External Electron Donor and with 1-Butene as Comonomer

[0055] The process conditions are given in Table 3 and the resin properties are given in Table 4. The molar ratio of TMA to titanium was 7.5. The molar ratio of $CHCl_3$ to titanium was 0.06. The molar ratio of THF to titanium was 3. Under these conditions a linear polyethylene free from agglomerate was withdrawn from the reactor at a rate of 200 1b/h. The productivity of the catalyst was 98 pounds of polyethylene per pound of prepolymer which corresponds to an activity of 210 grams polyethylene per millimole titanium per hour per bar of ethylene partial pressure.

[0056] The linear polyethylene had a density of 0.908 and a melt index $MI_{2.16}$, I_2, of 0.4 dg/min. The Melt Flow Ratio, I_{21}/I_2, was 28 and the ether extractables were 1.9 % by weight.

Table 3:

Reactor Conditions for Examples 5 through 7			
	Example		
	5	6	7
Reactor Pressure (psig)	294	297	297
Reactor Temperature (°C)	81	80	78
Fluidization Velocity (ft/sec)	1.96	1.97	1.93
Fluidized Bulk Density (lb/ft^3)	14.6	14.8	14.9
Reactor Bed Height (ft)	12	12	12
Ethylene (C_2) (mole%)	25	22	19
H_2/C_2 (molar ratio)	0.119	0.100	0.102
1-Butene/C_2 (molar ratio)	---	---	0.672
1-Pentene/C_2 (molar ratio)	---	0.447	---
1-Hexene/C_2 (molar ratio)	0.211	---	---
Co-catalyst	TMA	TMA	TMA
A1/Ti (molar ratio)	6	7	7.5
External Electron Donor	THF	THF	THF
THF/Ti (molar ratio)	3	3	3
$CHCl_3$/Ti	0.06	0.06	0.06
Production Rate (lb/h)	196	200	200
Space Time Yield (lb/h-ft^3)	3.56	3.70	3.73
Productivity (mass ratio)	168	129	98
Activity(g PE/mmoleTi-h-$bar_{ethylene}$)	259	239	210
Residual Titanium (ppm)	8.5	10.6	14

Table 4:

Resin Properties for LLDPE prepared in Examples 5 through 7			
	Example		
	5	6	7
Density (g/cc)	0.908	0.908	0.908
Melt Index, I_2, (dg/min)	0.6	0.5	0.4
Melt Flow Ratio (I_{21}/I_2)	34	31	28
Ether Extractables (wt %)	5.2	3.1	1.9
n-Hexane Extractable (wt%)	3.5	1.8	1.3
Dart Impact (g/mil)	>1500	>2000	950
MD_{TEAR} (g/mil)	700	550	313
TD_{TEAR} (g/mil)	750	470	323

[0057] A review of the data in Tables 3 and 4 allows the following observations to be made. As the olefin comonomer is reduced in length, for example 1-hexene to 1-pentene to 1-butene, the data shows that the molecular weight distribution as measured by melt flow rate (MFR) is decreased and the extractable content of the polyethylenes is also decreased.

EXAMPLE 8

Preparation of LLDPE with TMA as Co-Catalyst and with THF as External Electron Donor Utilizing a Ziegler-Natta Catalyst Added Directly to the Reactor

[0058] The process of Example 1 is followed with the exception that the Ziegler-Natta catalyst is directly injected into the reactor without having been converted to prepolymer form. A linear polyethylene is obtained.

[0059] Films prepared from the polyethylenes of the present invention are generally characterized as having improved strength properties which are particularly shown by the values of Dart Impact in Tables 2 and 4.

[0060] Articles such as molded items can also be prepared from the polyethylenes of the present invention.

[0061] It should be clearly understood that the forms of the invention herein described are illustrative only and are not intended to limit the scope of the invention. The present invention includes all modifications falling within the scope of the following claims.

Claims

1. A process for polymerizing ethylene and/or ethylene and at least one or more other olefin(s) comprising contacting, under polymerization conditions, the ethylene and/or ethylene and at least one or more olefin(s) with a Ziegler-Natta type catalyst, trimethylaluminum and tetrahydrofuran as external electron donor.

2. The process according to Claim 1 further comprising the presence of a halogenated hydrocarbon.

3. The process according to Claim 2 wherein the halogenated hydrocarbon is chloroform.

4. The process according to Claim 1 wherein the Ziegler-Natta type catalyst comprises a transition metal compound wherein the metal is selected from metals of Groups 4, 5, 6, 7, 8, 9 and 10 of the Periodic Table of the Elements, as defined herein.

5. The process according to Claim 4 wherein the metal of the transition metal compound is selected from the group consisting of titanium, zirconium, vanadium and chromium.

6. The process according to Claim 5 wherein the metal of the transition metal compound is titanium.

7. The process according to Claim 1 further comprising the presence of at least one internal electron donor.

8. The process according to Claim 1 further comprising the presence of magnesium and chlorine incorporated in the Ziegler-Natta type catalyst.

9. The process according to Claim 4 further comprising the presence of magnesium and chlorine incorporated in the Ziegler-Natta type catalyst.

10. The process according to Claim 7 further comprising the presence of magnesium and chlorine incorporated in the Ziegler-Natta type catalyst.

11. The process according to Claim 2 wherein the halogenated hydrocarbon is added in a molar ratio of halogenated hydrocarbon to transition metal component of the Ziegler-Natta type catalyst ranging from about 0.001:1 to about 1:1.

12. The process according to Claim 1 wherein trimethylaluminum is added in a molar ratio of trimethylaluminum to transition metal component of the Ziegler-Natta type catalyst ranging from about 1:1 to about 100:1.

13. The process according to Claim 12 wherein the molar ratio of trimethylaluminum to transition metal component of

the Ziegler-Natta type catalyst ranges from about 1:1 to about 50:1

14. The process according to Claim 1 wherein tetrahydrofuran is added in a molar ratio of tetrahydrofuran to transition metal component of the Ziegler-Natta type catalyst ranging from about 0.01:1 to about 100:1.

15. The process according to Claim 14 wherein the molar ratio of tetrahydrofuran to transition metal component of the Ziegler-Natta type catalyst ranges from about 0.1:1 to about 50:1

16. The process according to Claim 1 wherein the polymerization conditions are gas phase.

17. The process according to Claim 1 wherein the polymerization conditions are solution phase.

18. The process according to Claim 1 wherein the polymerization conditions are slurry phase.

19. The process according to Claim 1 wherein the at least one or more other olefin(s) is an olefin having 3 to 16 carbon atoms.

20. The process according to Claim 19 wherein the at least one or more other olefin(s) is selected from the group consisting of 1-octene, 1-hexene, 4-methylpent-1-ene, 1-pentene, 1-butene and propylene.

21. The process according to Claim 1 wherein the copolymer resulting from the polymerization of ethylene and at least one or more olefin(s) comprises ethylene in an amount of at least about 70% by weight of the copolymer.

22. The process according to Claim 1 wherein the Ziegler-Natta type catalyst comprises titanium, magnesium and chlorine.

23. The process according to Claim 22 further comprising the presence of a halogenated hydrocarbon.

24. The process according to Claim 22 wherein the polymerization conditions are gas phase.

25. A film fabricated from the polyethylene produced in accordance with Claim 1.

26. An article fabricated from the polyethylene produced in accordance with Claim 1.

Patentansprüche

1. Verfahren zum Polymerisieren von Ethylen und/oder Ethylen und mindestens einem oder mehreren anderen Olefin (en), umfassend das Kontaktieren unter Polymerisationsbedingungen des Ethylens und/oder des Ethylens und des mindestens einen Olefins oder der mehreren Olefine mit einem Katalysator vom Ziegler-Natta-Typ, Trimethylaluminium und Tetrahydrofuran als äußerem Elektronendonor.

2. Verfahren nach Anspruch 1, weiter umfassend die Anwesenheit eines halogenierten Kohlenwasserstoffs.

3. Verfahren nach Anspruch 2, in dem der halogenierte Kohlenwasserstoff Chloroform ist.

4. Verfahren nach Anspruch 1, in dem der Katalysator vom Ziegler-Natta-Typ eine Übergangsmetall-Verbindung umfasst, in der das Metall ausgewählt ist aus Metallen der Gruppen 4, 5, 6, 7, 8, 9 und 10 des Periodensystems der Elemente, wie hierin definiert.

5. Verfahren nach Anspruch 4, in dem das Metall der Übergangsmetall-Verbindung ausgewählt ist aus der Gruppe bestehend aus Titan, Zirconium, Vanadium und Chrom.

6. Verfahren nach Anspruch 5, in dem das Metall der Übergangsmetall-Verbindung Titan ist.

7. Verfahren nach Anspruch 1, weiter umfassend die Anwesenheit mindestens eines inneren Elektronendonors.

8. Verfahren nach Anspruch 1, weiter umfassend die Anwesenheit von Magnesium und Chlor, die dem Katalysator

vom Ziegler-Natta-Typ einverleibt sind.

9. Verfahren nach Anspruch 4, weiter umfassend die Anwesenheit von Magnesium und Chlor, die dem Katalysator vom Ziegler-Natta-Typ einverleibt sind.

10. Verfahren nach Anspruch 7, weiter umfassend die Anwesenheit von Magnesium und Chlor, die dem Katalysator vom Ziegler-Natta-Typ einverleibt sind.

11. Verfahren nach Anspruch 2, in dem der halogenierte Kohlenwasserstoff in einem Molverhältnis von halogeniertem Kohlenwasserstoff zu Übergangsmetall-Komponente des Katalysators vom Ziegler-Natta-Typ im Bereich von etwa 0,001 : 1 bis etwa 1 : 1 zugesetz wird.

12. Verfahren nach Anspruch 1, in dem Trimethylaluminium in einem Molverhältnis von Trimethylaluminium zu Übergangsmetall-Komponente des Katalysators vom Ziegler-Natta-Typ im Bereich von etwa 1 : 1 bis etwa 100 : 1 zugesetzt wird.

13. Verfahren nach Anspruch 12, in dem das Molverhältnis von Trimethylaluminium zu Übergangsmetall-Komponente des Katalysators vom Ziegler-Natta-Typ im Bereich von etwa 1 : 1 bis etwa 50 : 1 liegt.

14. Verfahren nach Anspruch 1, in dem das Tetrahydrofuran in einem Molverhältnis von Tetrahydrofuran zu Übergangsmetall-Komponente des Katalysators vom Ziegler-Natta-Typ im Bereich von etwa 0,01 : 1 bis etwa 100 : 1 zugesetzt wird.

15. Verfahren nach Anspruch 14, in dem das Molverhältnis von Tetrahydrofuran zu Übergangsmetall-Komponente des Katalysators vom Ziegler-Natta-Typ im Bereich von etwa 0,1 : bis etwa 50 : 1 liegt.

16. Verfahren nach Anspruch 1, in dem die Polymerisationsbedingungen eine Gasphase sind.

17. Verfahren nach Anspruch 1, in dem die Polymerisationsbedingungen eine Lösungsphase sind.

18. Verfahren nach Anspruch 1, in dem die Polymerisationsbedingungen eine Aufschlämmungsphase sind.

19. Verfahren nach Anspruch 1, in dem das mindestens eine oder die mehreren andere(n) Olefin(e) ein Olefin mit 3 bis 16 Kohlenstoffatomen ist.

20. Verfahren nach Anspruch 19, in dem das mindestens eine oder die mehreren anderen Olefin(e) ausgewählt sind aus der Gruppe bestehend aus 1-Octen, 1-Hexen, 4-Methylpent-1-en, 1-Penten, 1-Buten und Propylen.

21. Verfahren nach Anspruch 1, in dem das Copolymer, das aus der Polymerisation von Ethylen und mindestens einem oder mehreren Olefin(en) resultiert, Ethylen in einer Menge von mindestens 70 Gew.-% des Copolymers umfasst.

22. Verfahren nach Anspruch 1, in dem der Katalysator vom Ziegler-Natta-Typ Titan, Magnesium und Chlor umfasst.

23. Verfahren nach Anspruch 22, das weiter die Anwesenheit eines halogenierten Kohlenwasserstoffs umfasst.

24. Verfahren nach Anspruch 22, in dem die Polymerisationsbedingungen eine Gasphase sind.

25. Film bzw. Folie, hergestellt aus dem gemäß Anspruch 1 erzeugten Polyethylen.

26. Gegenstand, hergestellt aus dem gemäß Anspruch 1 erzeugten Polyethylen.

Revendications

1. Procédé pour polymériser l'éthylène et/ou l'éthylène et au moins une ou plusieurs autre(s) oléfine(s) comprenant la mise en contact, dans des conditions de polymérisation, d'éthylène et/ou d'éthylène et d'au moins une ou plusieurs oléfine(s) avec un catalyseur du type Ziegler-Natta, du triméthylaluminium et du tétrahydrofurane en tant

que donneur d'électrons externe.

2. Procédé selon la revendication 1, comprenant en outre la présence d'un hydrocarbure halogéné.

3. Procédé selon la revendication 2, dans lequel l'hydrocarbure halogéné est le chloroforme.

4. Procédé selon la revendication 1, dans lequel le catalyseur du type Ziegler-Natta comprend un composé d'un métal de transition, dans lequel le métal est choisi parmi les métaux des groupes 4, 5, 6, 7, 8, 9 et 10 de la classification périodique des éléments, telle que définie ici.

5. Procédé selon la revendication 4, dans lequel le métal du composé d'un métal de transition est choisi dans le groupe constitué par le titane, le zirconium, le vanadium et le chrome.

6. Procédé selon la revendication 5, dans lequel le métal du composé d'un métal de transition est le titane.

7. Procédé selon la revendication 1, comprenant en outre la présence d'au moins un donneur d'électrons interne.

8. Procédé selon la revendication 1, comprenant en outre la présence de magnésium et de chlore incorporés dans le catalyseur du type Ziegler-Natta.

9. Procédé selon la revendication 4, comprenant en outre la présence de magnésium et de chlore incorporés dans le catalyseur du type Ziegler-Natta.

10. Procédé selon la revendication 7, comprenant en outre la présence de magnésium et de chlore incorporés dans le catalyseur du type Ziegler-Natta.

11. Procédé selon la revendication 2, dans lequel l'hydrocarbure halogéné est ajouté en un rapport molaire entre l'hydrocarbure halogéné et le constituant métal de transition du catalyseur du type Ziegler-Natta compris entre environ 0,001:1 et environ 1:1.

12. Procédé selon la revendication 1, dans lequel le triméthylaluminium est ajouté en un rapport molaire entre le triméthylaluminium et le constituant métal de transition du catalyseur du type Ziegler-Natta compris entre environ 1:1 et environ 100:1.

13. Procédé selon la revendication 12, dans lequel le rapport molaire entre le triméthylaluminium et le constituant métal de transition du catalyseur du type Ziegler-Natta est compris entre environ 1:1 et environ 50:1.

14. Procédé selon la revendication 1, dans lequel le tétrahydrofurane est ajouté en un rapport molaire entre le tétrahydrofurane et le constituant métal de transition du catalyseur du type Ziegler-Natta compris entre environ 0,01:1 et environ 100:1.

15. Procédé selon la revendication 14, dans lequel le rapport molaire entre le tétrahydrofurane et le constituant métal de transition du catalyseur du type Ziegler-Natta est compris entre environ 0,1:1 et environ 50:1.

16. Procédé selon la revendication 1, dans lequel les conditions de polymérisation sont une polymérisation en phase gazeuse.

17. Procédé selon la revendication 1, dans lequel les conditions de polymérisation sont une polymérisation en solution.

18. Procédé selon la revendication 1, dans lequel les conditions de polymérisation sont une polymérisation en suspension.

19. Procédé selon la revendication 1, dans lequel la(les) au moins une ou plusieurs autre(s) oléfine(s) est(sont) une (des) oléfine(s) ayant 3 à 16 atomes de carbone.

20. Procédé selon la revendication 19, dans lequel la(les) au moins une ou plusieurs autre(s) oléfine(s) est(sont) choisie(s) dans le groupe constitué par le 1-octène, le 1-hexène, le 4-méthylpent-1-ène, le 1-pentène, le 1-butène et le propylène.

21. Procédé selon la revendication 1, dans lequel le copolymère résultant de la polymérisation d'éthylène et d'au moins une ou plusieurs oléfine(s) comprend de l'éthylène en une quantité égale à au moins environ 70% en masse du copolymère.

22. Procédé selon la revendication 1, dans lequel le catalyseur du type Ziegler-Natta comprend du titane, du magnésium et du chlore.

23. Procédé selon la revendication 22, comprenant en outre la présence d'un hydrocarbure halogéné.

24. Procédé selon la revendication 22, dans lequel les conditions de polymérisation sont une polymérisation en phase gazeuse.

25. Film fabriqué à partir du polyéthylène produit selon la revendication 1.

26. Objet fabriqué à partir du polyéthylène produit selon la revendication 1.